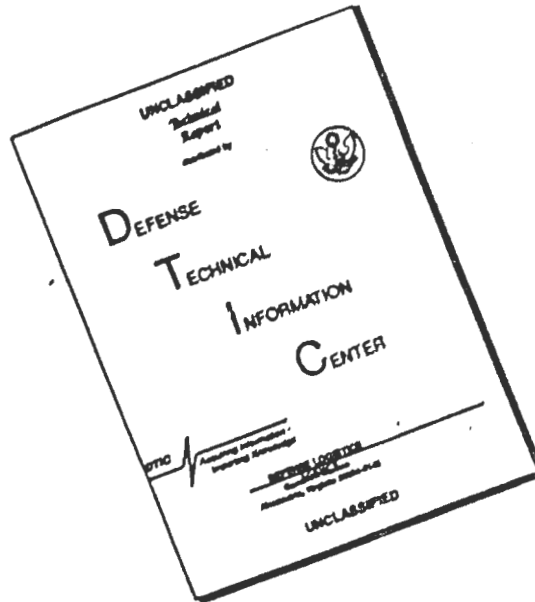# DISCLAIMER NOTICE

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THERMAL BEHAVIOR AND MELTING

OF

NON-IONIC DYE SOLIDS

by

Francis Jones

and

Leonard J. Flores

November 1970

UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

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13. ABSTRACT

The physico-thermal process occurring in pure disperse and vat dye solids on heating up to the melting or decomposition point of the dye has been examined. Differential scanning calorimetry has been used to detect and characterize solid→solid and solid→liquid phase changes by determining heats and entropies of transition and melting. The existence of polymorphs and associated thermal transitions has been shown by hot-stage microscopy, photomicrography, and X-ray powder diagrams. The calorimetric method has also been used to determine the temperature dependence of the heat capacity of the dyes. In those dyes exhibiting a solid→liquid phase change, evidence of pre-melting or premonitory effects are observed from which the activation energy of disorder formation in the crystal has been found. With vat dyes, which do not melt within the temperature range considered, there is evidence for an increase in lattice perfection at high temperature without change in lattice structure. The results may be usefully applied to dyeing processes both under aqueous and anhydrous conditions.

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Heating	8		10		6	
Dyes	1		1		7	
Melting	4		8		6	
Decomposition	4		8		6	
Crystal structure					7	

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TECHNICAL REPORT
71-52-CE

THERMAL BEHAVIOR AND MELTING OF NON-IONIC DYE SOLIDS

by

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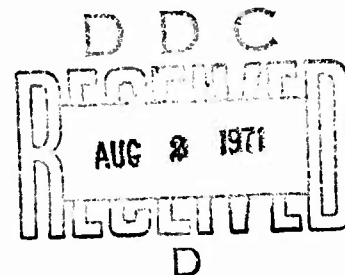
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Clothing and Personal Life Support Equipment Laboratory
U. S. ARMY NATICK LABORATORIES
Natick, Massachusetts 01760

FOREWORD

The Visiting Scientist Research Associateships Program administered by the National Academy of Sciences permits an infusion of new ideas, approaches and talents into the NLABS program. The subject matter in the research undertaken by the scientist is usually one of his own choosing with specific relevance to the mission of the Laboratories. In the present instance, the choice of subject has broad scope relatedness not only to several areas of concern to the Army but has broader implications in the civilian sector. With the increased use in military clothing of fibrous systems that are difficult to dye from aqueous media and which are amenable to vapor phase techniques, the implications of the studies reported here become truly significant. The fact that the scientist came from a foreign university also added to the value of the program in that there was an opportunity for exchange and cross-fertilization, considerations that form a good foundation for mutual understanding and for progress. The junior author of this report was detailed from his normal duties in the Test Methods Development Branch, TR&ED, C&PLSEL, to assist the senior scientist in this work. Mr. Frank Rizzo served as Scientific Advisor.

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ABSTRACT

The physico-thermal process occurring in pure disperse and vat dye solids on heating up to the melting or decomposition point of the dye has been examined. Differential scanning calorimetry has been used to detect and characterize solid→solid and solid→liquid phase changes by determining heats and entropies of transition and melting. The existence of polymorphs and associated thermal transitions has been shown by hot-stage microscopy, photomicrography, and X-ray powder diagrams. The calorimetric method has also been used to determine the temperature dependence of the heat capacity of the dyes. In those dyes exhibiting a solid→liquid phase change, evidence of pre-melting or premonitory effects are observed from which the activation energy of disorder formation in the crystal has been found. With vat dyes, which do not melt within the temperature range considered, there is evidence for an increase in lattice perfection at high temperature without change in lattice structure. The results may be usefully applied to dyeing processes both under aqueous and anhydrous conditions.

INTRODUCTION

In the technical application and manufacture of dyes and pigments which do not contain water-solubilizing groups, there is a growing awareness that differences in properties of solid particles, particularly color, may be due not only to particle morphology and size, but also to the existence of crystal structures which may differ from each other but which derive from the same compound. Linear quinacridones, indanthrone, indigo and thioindigo are examples which may show differences in shade and in other properties, depending upon the conditions during the final stages of manufacture or during their application.

Although crystal structures of simple azobenzene derivatives (1) and anthraquinonoid dye intermediates such as 1,5-dinitro-4,8-dihydroxy-anthraquinone, N,N'-diphenyl-1,5- and N,N'-diphenyl-1,8-diaminoanthraquinone (2) have been routinely investigated by X-ray diffraction methods, little reference has been made to the possibility that the crystals examined may exist in metastable or stable forms. The opinion has been expressed (3) that routine analyses of this type must give way to structure analyses made at various temperatures or pressures or under other changed or changing conditions which occur in different crystallization or precipitation processes. The fact that copper phthalocyanine and platinum phthalocyanine both exist in different structural forms which are stable at room temperature has however been taken into account (4) in more recent structural determinations.

The main purpose of the present research, in this context then, is to determine whether the existence of different structural forms of dyes and pigments can be shown to occur using means which do not involve a full X-ray structural investigation and to determine whether changes in form can be induced by thermal treatment.

Polymorphism

The occurrence of more or less stable crystal structures of a substance is known as polymorphism and the change from one crystal structure to another is known as a polymorphic transition or transformation. The ability to crystallize as more than one distinct crystallographic entity is best illustrated by the structures of carbon as diamond or as graphite. Differences in structure lead to differences in properties and in commercial products to differences in performance. It is for this reason that competitive industry publishes research on this topic only at infrequent intervals.

Most compounds, both inorganic and organic are polymorphic, although the preparation of some polymorphic modifications may be difficult or impossible to realize in practice. It must be pointed out that crystals possessing different habit or shape (which can also lead to differences in the visual appearance of solids) are not necessarily polymorphic. Crystals of different habit but of the same crystallographic arrangement

always have the same angle between the same faces whereas crystals of poly-
morphs of the same compound also exhibit different angles. Since the phen-
omenon is dependent upon differences in lattice arrangements, any process
which destroys the crystal lattice may be used to induce different crystal
forms. Under conditions such as melting, vaporization or solution of
the solid the lattice arrangement of molecules becomes disordered or random.
By inducing order into such a random system through crystallization from
solution or melt, or direct condensation to solid from vapor, the new
lattice arrangement may differ from the original. Similarly, by crystal-
lizing from the same solvent under different conditions, at different
rates for example, or by crystallizing from different solvents, new forms
of crystals may be obtained. It becomes obvious then that the conditions
and methods employed in the last stages of the technical manufacture of
dye solids, such as crystallization, chemical reaction and precipitation,
or salting out, will determine whether the dye solid obtained is one
modification or another. Changes of a physical nature could also occur
during drying and grinding processes, dyeing and any heat-treatment process.
It is the latter process with which we are concerned in this research.

a. Classification of Polymorphic Transitions

In addition to obtaining polymorphs through phase changes the supply
of energy in the form of heat can lead to transitions in which no obvious
visible phase change can be detected. It is useful therefore to attempt
to characterize all the mechanisms by which transitions may arise.

In all cases it is necessary to supply energy to the solid. The trans-
ition may result from dilation or distortion of the lattice network to
form a new arrangement. This type of transition may not involve any inter-
molecular bond breakage and consequently the re-arrangement may occur
rapidly. The disorder induced in the solid may represent rotational disorder
of the molecules in which the molecules move about their mean positions in
the network. Some of the weaker bonds between molecules are broken while
stronger bonds are retained. Greater energies are required to effect
transformations in which the lattice network is broken and re-formed in
a new arrangement. In some cases this bond energy within the lattice may
be greater than that required to break interatomic bonding in the molecule
and decomposition may occur at lower temperatures than transition. It
is interesting to observe that indigo crystals decompose to give a product
in which the original crystal morphology is retained.

The classification of transition mechanisms has been carried out by
Buerger (5) on the basis of structural changes, but, as McCrone (6) points
out, there appears to be no clear-cut classification. An alternative (7)
is to consider the transitions as first- or second-order. At constant
pressure, both first and second order transitions possess a continuous
free energy curve when plotted against temperature. The distinction between
orders is that the enthalpy $(H-H^o)$ or entropy (S) curves are discontinuous,
with an isothermal discontinuity for a first-order transition, and continuous

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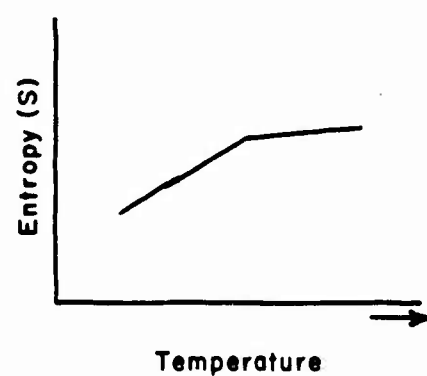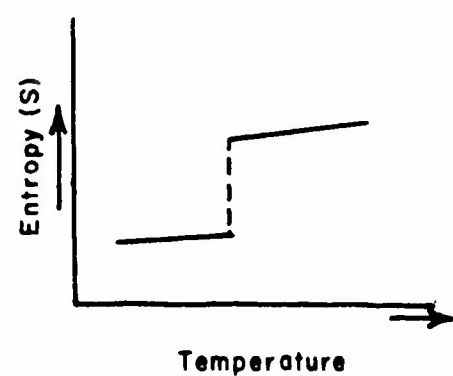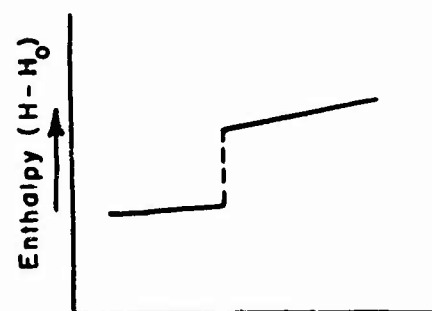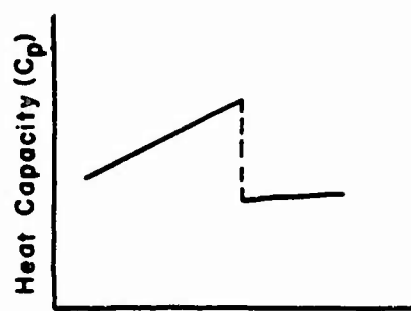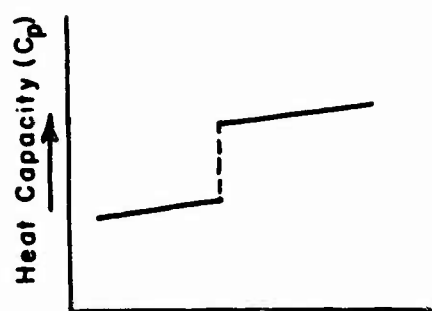
Figure I. HYPOTHETICAL FIRST- AND SECOND-ORDER TRANSITIONS

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for a second-order transition. The differences are shown in Figure 1. Heat capacity (Cp) changes are discontinuous for both first- and second-order transitions. It is assumed that the two solid phases in a thermo-dynamical treatment of this kind are separate and distinct. Thus, an isothermal change occurs in the entropy at a specific temperature in a first-order transition, as shown in Figure 1a.

Many transitions, however, occur over a range of temperatures even when thermal equilibrium has been attained, and Ubbelohde (8) suggests that the concept of two distinct phases may break down in the transition region.

A more empirical or phenomenological approach to the classification of transitions has been taken by McCullough (9) in which the shapes of the heat capacity-temperature curves are utilized. Figure 2(a) represents an ideal system in which the heat capacity changes for both a transition at $T_{II \to I}$ and melting at T_m occur isothermally, and in which at other
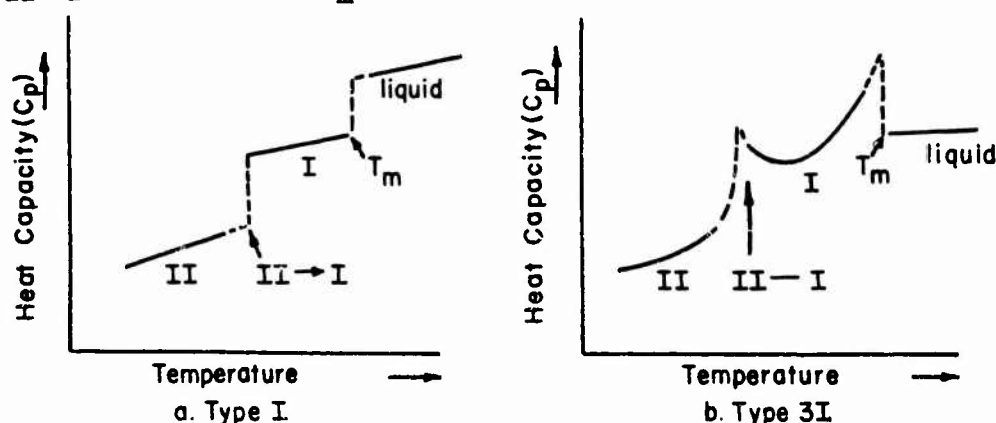
Figure 2. PHASE TRANSITIONS IN HEAT CAPACITY-TEMPERATURE RELATIONS

temperatures there is a normal linear relation between C_p and temperature. Type 1 transitions are defined by this linear relation occurring over the whole temperature range. The type 3I transition shown in Figure 2(b) demonstrates a curve which is non-linear, in which a "pre-transition" or "fore-warning" effect is observed in both Phase I and Phase II showing that the transition II→I commences before the transition temperature and continues after the transition temperature has been reached. The 3I transition shows a non-linear relation both before and between transition temperature and melting temperature. The more familiar "lambda" curve in which the transition may be classified by a continuously changing heat capacity with a maximum or peak, is referred to as Type H. As many as seven different classes of transitions may be recognized.

b. Characterization of Polymorphic Transitions

Since polymorphism arises from the existence of different crystallographic

structures of the same element or compound, a direct verification can be obtained by X-ray diffraction techniques, either by the powder method (10) or by rotation photographs of single crystals (8).

Other methods of characterization which measure changes in those properties of solids that are dependent upon the forces existing between entities situated at lattice sites in the crystal are also used. The methods are indirect but extremely useful. They include adiabatic calorimetry, inelastic neutron scattering, the measurement of vapor pressure of solids, molal volume, thermal expansion, compressibility and thermal conductivity. Changes in heat capacity with temperature and latent heat measurements are particularly useful since they allow enthalpy and entropy changes to be calculated. Westrum and McCullough (11) have given a comprehensive survey of the changes in properties of organic solids on heating, with particular emphasis on heat capacity changes as measured by adiabatic calorimetry. This general method, however, requires the attainment of thermal equilibrium at each temperature studied and is, of necessity, slow. More rapid methods which are equally informative but much less precise, since they rely on non-equilibrium or dynamic measurement, are differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

A DTA apparatus measures the difference between the temperature of a sample in a cell and the temperature of a thermally inert reference material and records the difference against time or temperature. When the apparatus is operated as a differential scanning calorimeter the sample and its container are maintained at the same temperature as the reference material and its container. In this mode, when an exothermic or endothermic reaction takes place, there is an exact compensation of energy supplied as electrical energy to the reference container. The area enclosed by the endothermic or exothermic peak and the base line, when this energy change is recorded against temperature, is therefore a direct measure of the heat liberated or absorbed by the sample if the thermal resistance of the sample is assumed negligible. Since this method was used in the present research the general theory of DTA, which applies equally well for DSC, is given below.

c. General Theory of Thermal Energy Flow

Consider a sample and its container at temperature T_s, as shown in Figure 3 with a thermal energy source at T_p, and a path having a thermal resistance R, through which thermal energy flows to or from the sample at a rate of dq/dt. Both sample and container are at temperature T_s, the thermal resistance R is constant over the temperature range considered, and the total heat capacity of sample and container is C_s. Heat generated by the sample, dh/dt per unit time is, by convention, positive and heat absorbed is negative. The heat flow from T_p to the sample is positive.

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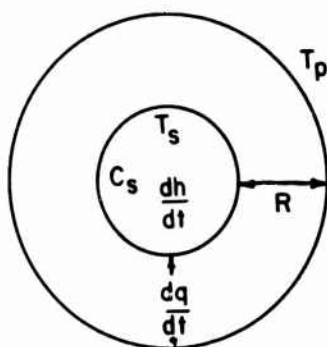
Figure 3. THERMAL ENERGY FLOW RELATIONS IN DSC

If a sample generates energy at a rate dh/dt the sample will either increase its temperature or dissipate its excess energy to the surroundings. The sum of these two effects must equal dh/dt, i.e.,

$$\frac{dh}{dt} = \frac{C_s dT_s}{dt} - \frac{dq}{dt} \tag{1}$$

The rate of heat loss to the surroundings is governed by the thermal resistance R and the temperature difference, i.e.,

$$\frac{dq}{dt} = \frac{T_p - T_s}{R} \tag{2}$$

Substituting for dq/dt in equation (1),

$$\frac{dh}{dt} = \frac{C_s dT_s}{dt} + \frac{T_s - T_p}{R} \tag{3}$$

Similarly by considering the reference sample at temperature T_r,

$$\frac{dh}{dt} = \frac{C_r \, dT_r}{dt} + \frac{T_r - T_p}{R} = 0 \tag{4}$$

since zero energy is emitted by the inert reference. By subtracting (4) from (3) and rearranging, we obtain,

$$\frac{R dh}{dt} = T_s - T_r + \frac{R(C_s - C_r) dT_r}{dt} + \frac{RC_s d(T_s - T_r)}{dt} \tag{5}$$

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The thermal resistance R is assumed the same for both sample and reference. In the steady state when the scanning rate dT_r/dt is constant and $dh/dt = 0$ since no thermal event is taking place, and $T_s - T_r$ is constant, equation (5) reduces to,

$$T_s - T_r = -R(C_s - C_r)\frac{dT_r}{dt} \qquad (6)$$

This condition is illustrated as the baseline displacement of the zero signal level in Figure 4.
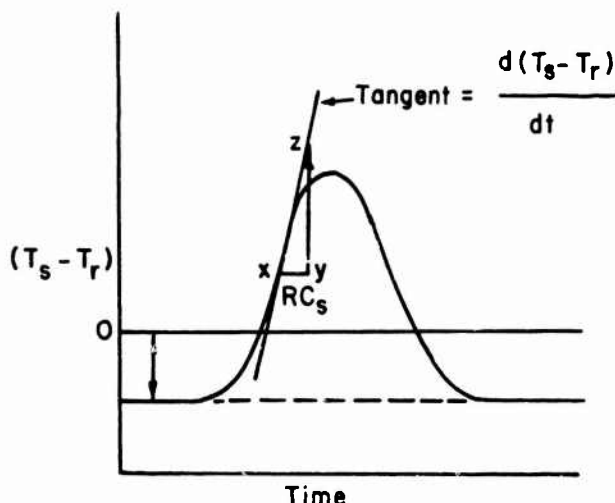
Figure 4. VARIATION OF TEMPERATURE DIFFERENCE WITH TIME

The third term in equation (5) must be considered when a thermal event is occuring, and is the slope of the curve at any point multiplied by the constant RC_s. Since the slope at point x is the tangent $d(T_s - T_r)/dt$, the third term is equivalent to the vertical height yz shown in Figure 4 and may be determined if RC_s is known.

In DSC methods the exact compensation of energy supplied as electrical power is equivalent to measuring dq/dt in equation (1) and from the first time derivative of equation (2) a basic equation similar to (5) can be obtained for DSC, i.e.,

$$\frac{dh}{dt} = \frac{-dq}{dt} + \frac{(C_s - C_r)dT_p}{dt} - RC_s\frac{d^2q}{dt^2} \qquad (7)$$

The terms on the right hand side of (7) represent the signal measured from zero (I in Fig. 5), the baseline displacement due to heat capacity difference between sample and reference (II) and the slope of the recorded curve multiplied by RC_s (III), respectively.

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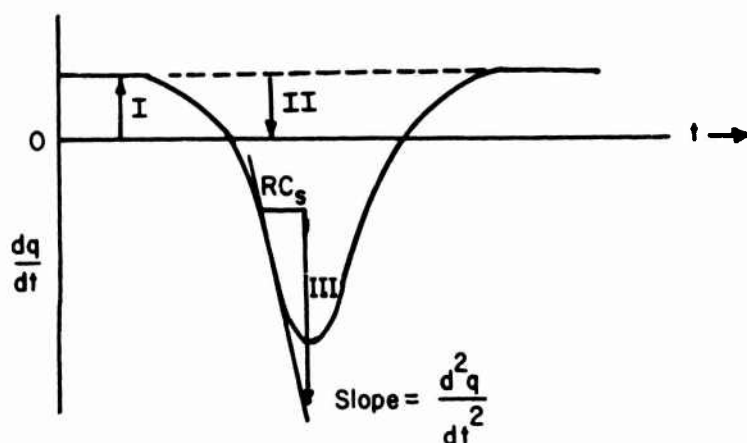
Figure 5. VARIATION OF HEATING (COOLING) RATE OF SAMPLE WITH TIME

The thermal resistance (R) in differential scanning calorimetry occurs only in the third term of equation (7) and it is therefore possible to reduce the thermal time constant RC_s by reducing R without sacrificing sensitivity so that, in the limit, the slope at any point represents the true thermal behavior of the sample without any thermal lag.

The area under a DSC curve is equivalent to Δq and since $\Delta q = -\Delta h$ the heat content change of the sample, Δh, can be obtained by determining the area under the curve when a standard calibrating substance such as a pure metal of known heat of fusion is used. Since R need not be known nor need it be constant, a single calibration is sufficient for the whole temperature range. The calibration coefficient in DSC to convert areas to calories is an electrical conversion factor. In quantitative DTA it is a thermal coefficient which varies with temperature.

Heat capacity at constant pressure, C_p, can be determined by DSC by obtaining a baseline plot using two empty containers. The displacement from the zero line indicates the difference in heat content of the two containers. By repeating the same procedure under the same conditions with the sample in the sample container the recorded differential temperature will be directly proportional to the heat capacity of the sample after correction for container differences. Changes in heat capacity with temperature can thus be observed.

It must again be emphasized that the data obtained are results of non-equilibrium or dynamic experiments. Since transition temperatures are dependent to a greater or lesser extent on heating rate the results at best can only be obtained within an accuracy of $\pm 5.0\%$. The method in

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the first place is justified if only because of the lack of data on heat capacity of dye solids.

d. Polymorphism in Dyes and Pigments

Von Susich (12) was one of the first to show that X-ray diffraction of dye solids could be used as a means of identifying unknown dyes provided sufficient data were available on known dyes to allow comparisons to be made. He was careful to point out that the comparison should be made only when both dyes exist in the same structural modification. Válko (13) had earlier shown that vat dye crystals, formed on oxidation and/or soaping of heavily dyed films, could be detected by X-ray diffraction. Von Susich also examined dyeings of Indanthren Brilliant Scarlet RK, C.I. 68300, which changed in color from orange to scarlet on soaping with the development of crystals within the substrate. Although no comment is made on this point, the X-ray diffraction patterns show that these crystals differ from the type observed in the commercial powder of this vat dye.

Previously, it had been shown (14) that Indanthrone, C.I. 69800,

C.I. 69800
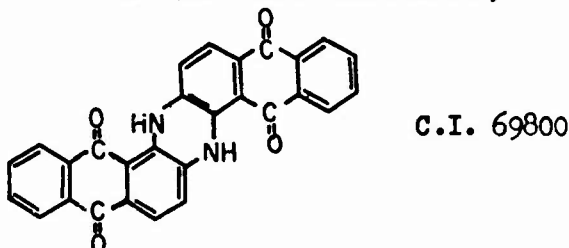
could exist in four different forms. These were prepared by solution and subsequent precipitation or crystallization. The three metastable polymorphs could all be converted to the more stable α-form on heating to 250°C. The existence of four polymorphs of this compound has since been disputed by Warwicker (15) who claimed from X-ray data that only the α- and δ-forms described by Von Susich existed. Other vat dyes examined by Warwicker included pyranthrone, C.I. 59700, and 16, 17-dimethoxyviolanthrone, C.I. 59825.

C.I. 59700

C.I. 59825
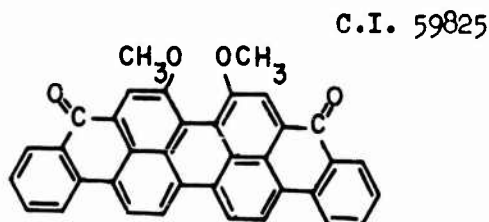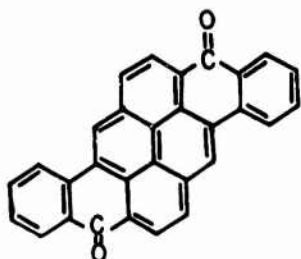
The latter, Caledon Jade Green, possessed a completely different structure after a long period in storage in comparison with an old sample, freshly crystallized from pyridine. It was assumed that on storage a slow transition to a more stable form occurred, or that an additional form of this

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dye was possible. It is noticeable that in this and other more recent work (16) attempting to substantiate the existence of four polymorphs of 6,6'-diethoxythioindigo, C.I. 73335, by X-ray diffraction, each form is

C.I. 73335
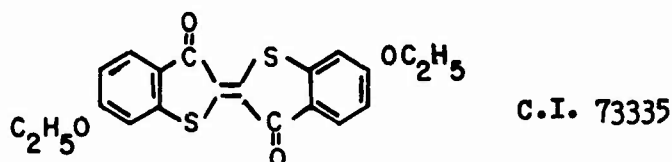
obtained by a phase change in which the lattice structure is destroyed and then reformed by a crystallization or precipitation process. No evidence, apart from the phase change in Indanthrone, has been presented to show whether thermal factors alone can induce transitions in the solid phase. Polymorphism in disperse azo dyes and azo pigments has been studied to a lesser extent. Modifications are usually obtained by varying pH conditions in the coupling of the diazotized amine. By coupling diazotized Tobias acid to 2-naphthol to give C.I. Pigment Red 49 (C.I. 51630) as the sodium salt, within the pH range 9-13, as many as four

C.I. 51630

polymorphs have been reported (17). Also marked changes in habit of crystals of C.I. Disperse Yellow 3, have been observed (18) with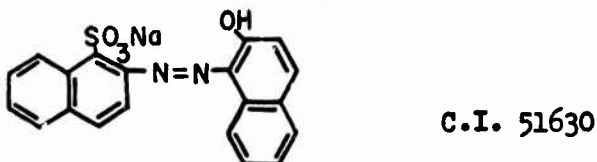 different coupling conditions, but verification that the dye may also exist in different structural modifications was not obtained.

It is well known that many disperse dyes can undergo crystal growth during dyeing. It is usual to attribute such growth to the difference in solubility between small and large particles, the latter growing at the expense of the former. The possibility of nucleation and growth of other structural forms must always be considered. The presence of more than one modification in dyebaths of C.I. Disperse Yellow 3 has been shown by Jones (19). Similarly, anomalous results in the rates of dyeing of poly-ester material with four pure dyes which had been pretreated in boiling water, and which had been interpreted as being due to changes in crystal size (20), could equally well have been interpreted in terms of the presence of different structural modifications. Finally, a mono-azo disperse dye has recently been prepared (21) in a number of structural forms sufficiently stable to be applied to fibers from aqueous dispersions. It is interesting to observe that each form gives a different saturation equilibrium value within the fiber, a value which up to recently has been considered as a thermodynamic constant in the dyeing theory of disperse dyes.

On reviewing the information up to this point, it is obvious that there is a lack of calorimetric data available on dye solids. Also, and in view

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of the planar shape of these dye molecules with their greater tendency to stacking arrangements within the crystal, transformation may only occur through higher energy molecular randomization and re-formation processes. It was the purpose of this project then, to obtain calorimetric data on dye solids over a range of temperatures. Deviations from linear behavior, e.g., in heat capacity, on heating to the melting point, may indicate changes in crystal structure caused by migration of voids within the lattice or by the partial collapse of the lattice leading to increases in the degree of disorder.

EXPERIMENTAL

The dyes shown in Table I were chosen on grounds of availability and are considered to be representative of their chemical class for use as disperse or vat dyes. Dyes I, II and III were supplied as press-cake from the manufacturer (Yorkshire Dyeware Co., Ltd., U. K.), IV as a commercial dye powder, Latyl Yellow YLW (Du Pont) and dyes V, VI, and VII as the solublized leuco-ester of the corresponding indigoid or thio-indigoid derivative, i.e., Algosol Blue OCG, Algosol Orange HRCF and Algosol Brown IBRD (GAF Corp.), respectively.
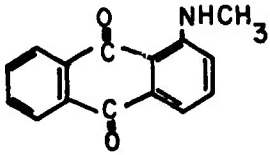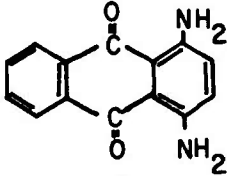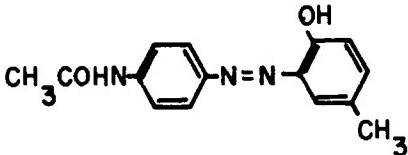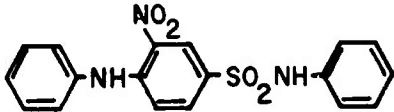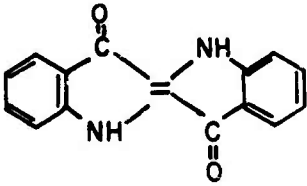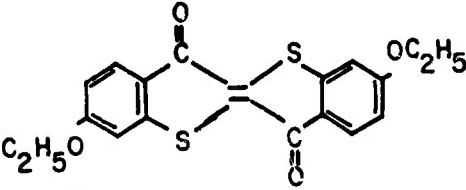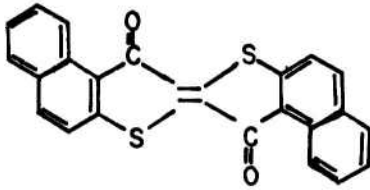
a. Purification of Dyes

Purification of dye samples is necessary since the presence of impurities can affect the type of modification produced and its physical behavior. Of a number of vat dyes of different chemical classes which were examined, the most easily purified were the indigoid and thioindigoid derivatives. Conventional vat dyes similar in chemical structure to Indanthrone, for example, were difficult to recrystallize from polar solvents without the possibility of solvent occlusion. In consequence of this, the use of sulphuric acid as a solvent, with the attendant risk of sulphate formation, was avoided. Also, the reduction and re-oxidation of vat dyes in aqueous media, again with the possibility of inorganic occlusion, was not pursued, and vat dyes of high molecular weight were not examined further.

Twenty-five grams of the crude press-cake of dyes I, II and III, were each extracted with 500 ml boiling distilled water to remove water soluble matter. Dye I was recrystallized from n-butanol to constant melting point and given a final wash with cold ethanol to remove n-butanol. Disperse Violet 1, using acetone as solvent, could not be obtained sufficiently pure using recrystallization procedures. A solution was therefore chromatographed using an alumina column with benzene as solvent and a benzene/acetone, 3:1 (v/v) mixture as eluent. At least three colored impurities were removed by this method, even though the dye had previously been recrystallized to constant m.p. After chromatography, the dye was finally recrystallized from a benzene/acetone 3:1 (v/v) mixture. Dye III was treated as Dye I, also using benzene as the solvent. Disperse Yellow 42 (IV) as commercial powder, was extracted with acetone in a Soxhlet extractor and recrystallized from this solvent to constant m.p.

Commercial samples of vat dyes V, VI and VII were purified in an identical manner as follows:

Two grams of the sulphuric acid ester of the leuco dye were dissolved in 200 ml distilled water at room temperature and the solution filtered. Two ml 10% HCl was added dropwise with gentle but efficient stirring to give a solution of pH 2-3, followed by dropwise addition of a 0.5% solution of aqueous sodium nitrite

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TABLE I - DYES USED

Dye No.	Classification C.I. (Part I) No.	Formulae	Solvent
I	Disperse Red 9		n-butanol
II	Disperse Violet 1		benzene/acetone (3:1 by vol.)
III	Disperse Yellow 3		benzene
IV	Disperse Yellow 42		acetone
V	Vat Blue 1		nitrobenzene
VI	Vat Orange 5		nitrobenzene
VII	Vat Brown 5		nitrobenzene

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until precipitation of the oxidized vat dye was completed. The suspension was filtered, testing the filtrate with sodium nitrite solution. The sample was then washed neutral with cold distilled water and finally with methanol and dried at < 60°C.

Each vat dye was then recrystallized twice from pure nitrobenzene, the crystals being finally washed well with methanol to remove residual nitrobenzene. At each purification step, with all dyes, thin layer chromatography using Eastman Chromatogram Sheet 6060 (silica gel on polyester film) pre-dried at 60°C was carried out. Disperse dyes were spotted on sheet using acetone solutions and developed with benzene/ acetone 4:1 (v/v) mixtures and vat dyes were spotted and eluted with nitrobenzene. Purity was regarded as adequate when only one spot could be developed on the chromatogram.

b. Methods and Procedure

(1) Since it is the purpose of this research to examine physico-thermal behavior of the dyes in atmospheric conditions, a Du Pont 900 Differential Thermal Analyzer was used, operating with a differential scanning calorimeter attachment. In this method it is possible, after calibration with a substance of known latent heat of fusion, to determine quantitatively any solid state transition or melting phase-change occurring in the dye. Samples of the same dye, prepared as different structural modifications can also be compared.

(2) The dye solid during the course of heating or cooling cannot be observed in the calorimeter and a parallel investigation using a Thomas polarizing microscope fitted with a Kofler hot-stage was carried out, using, as closely as possible, the same heating rates as those obtained with the DSC apparatus.

(3) Heat capacity determinations for each form of the dye over the same temperature ranges as in (1) were also determined using the DSC apparatus.

(4) X-ray diffraction data for different structural forms were obtained.

(5) Some evidence of structural modifications obtained in the presence of dispersing agents in aqueous dispersions is also given.

Each of these sections is described in more detail below.

Differential Scanning Calorimetry. A brief survey of the theory of differential thermal analysis and differential scanning calorimetry has been given in the Introduction. Figure 6 shows a diagrammatic cross-section of the DSC cell used in this work. A Chromel wire is welded to the center of each raised platform of a Constantan disc providing
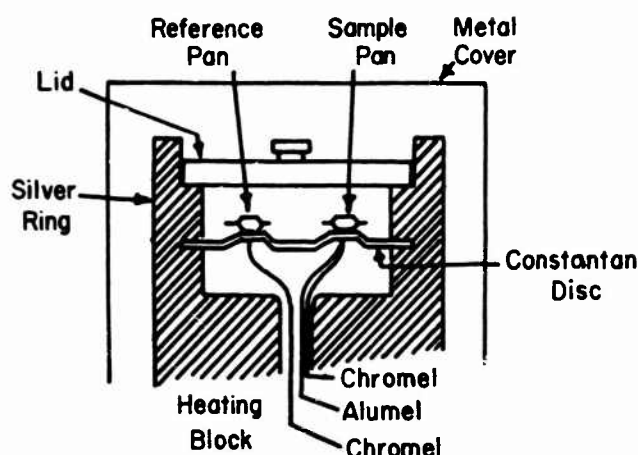
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Figure 6. DSC CELL CROSS-SECTION

thermocouple junctions in direct contact with the reference and sample
pans to measure the differential temperature. The temperature of the
sample is determined by a Chromel-Alumel thermocouple junction welded to
the center of the sample platform. In addition to its use as thermo-
couple junctions for measuring temperature, the Constantan disc serves
as the heat source for the sample and reference pans by acting as the
thermal path from the heating block. Radiation cooling effects are minimized
by provision of a silver ring and lid surrounding the sample and reference
chamber. The whole is covered by an inverted metal (steel) cover and
protected from draughts by an inverted bell-jar.

Calibration of Instrument. Since the thermocouples in the DSC
cell do not penetrate the sample, the peak temperature for a thermal event
differs from the peak temperature determined by DTA mode in which thermo-
couples are embedded in sample and reference held in capillary tubes.
It has been found (22) that the extrapolated onset-temperature in a DSC
cell corresponds to the peak temperature of a DTA cell, but there is only
a slight difference for small samples. All temperatures were therefore
considered to be peak temperatures. In quantitative work, all samples
for calibration and all dyes were weighed on a Cahn RG Electrobalance in
tared sample containers with an accuracy of ± 0.01 mg. The balance was
used as a null-point instrument by connecting the recorder out-put to a
Leeds & Northrup galvanometer.

The areas under peaks were obtained by means of a Keuffel and
Esser Co. Planimeter No. 4230 taking the mean value of at least six
determinations of area in each case.

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The mean calibration factor (E) for the instrument to determine heats of fusion or transition was obtained using supplied samples of indium and tin, and using the procedure laid down in the instrument instruction manual as follows:

Approximately 15 mg metal sample, M, in a sealed pan is heated at a rate, a, of 10°C/min. with a Y-axis sensitively, ΔT_s, of 1°C/in. and an X-axis sensitively T_s of 20°C/in. Knowing the area under the curve (A) and from the known heats of fusion, ΔH_f, the calibration factor can be obtained from the expression:

$$E = \frac{\Delta H_f M a}{A \Delta T_s T_s} \tag{8}$$

Table II gives values of E determined in this way, from which the mean calibration factor is found to be 130.7 mcal/°C/min.

TABLE II - CALIBRATION FACTORS

Metal	ΔH_f* cal/gm.	M mg.	Area in.^{2}	E mcal/°C/min.
Indium	6.79	16.00	0.42	129.33
		16.00	0.42	129.33
Tin	14.20	15.03	0.82	130.13
		15.03	0.81	131.74
		14.78	0.79	132.80

*American Institute of Physics Handbook

Typical traces obtained for these two metals at the melting point are shown in Figure 7.
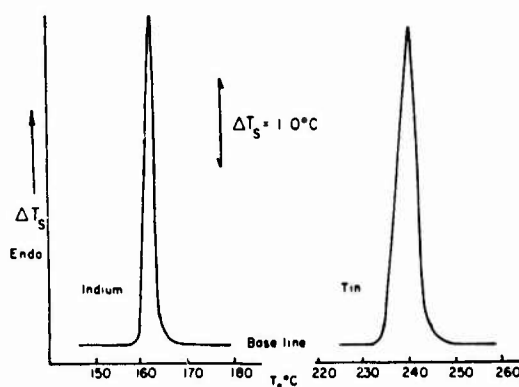

Figure 7 CALIBRATION THERMOGRAMS FOR INDIUM AND TIN

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Optical Examination. All dye solids were examined by hot-stage microscopy using a Kofler-Thomas hot-stage microscope operating at an approximate magnification of X200. Thermometers were calibrated against the melting points of pure test substances supplied. The micrscope was unsuitable for photography. All photographs were obtained with a 35 mm camera fitted to a Bausch and Lomb "Microzoom" Model H binocular microscope. Exact magnification was measured from photomicrographs of a one mm scale divided into 100 divisions. Kodak "Plus-X" panchromatic film, speed 125 ASA was used in conjunction with a Bausch and Lomb 0.7 neutral filter with a light source setting of 4. Exposure times for low power (X260 on photographs shown) and higher power (X530) were 1/25 and 1/10 sec., respectively.

Dry samples of dye crystals were placed between the slide and a cover slip. Where there was any obscuring tendency by sublimation of volatile dye on to the cover slip, the latter was removed before heating. Melted samples were allowed to cool naturally before examination of the re-crystallized melt.

Specific Heats - Calibration. In determining specific heats of unknown substances the value of E, for greatest accuracy, should be determined by calibration using known data for the calibrating substance. We have found, however, that the value of E determined from known heats of fusion of metals gives values for specific heat which are comparable with literature data shown in Table III.

The method described briefly in the Introduction (page 8) requires the establishment of an initial thermal equilibrium position in which the reference pan and the unsealed sample pan temperatures are maintained constant at zero differential temperature (point A - Fig. 8). After thermal equilibrium has been reached, the cell is heated at a
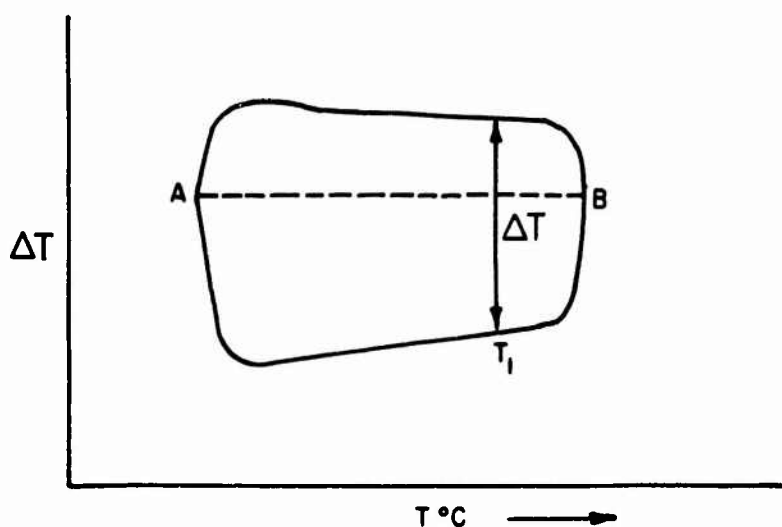

Figure 8. DETERMINATION OF SPECIFIC HEATS

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predetermined rate, usually 20°C/min. over the temperature range required. The pans are again brought to thermal equilibrium at point B. The deflection of the curve over this range is due to differences in heat content of the two containers. After addition, weighing and sealing of the test sample in its container the procedure is repeated to give the lower curve in Figure 8. The specific heat of the test sample at constant pressure in cal/gm/°C at temperature T_1 is given by the expression:

$$C_p = \frac{\Delta T \times E}{M \times a} \qquad (9)$$

where E is the previously determined calibration factor, M is the mass of sample and a is the heating rate. Calibration runs carried out with pure samples of zinc, Atomic Wt., 65.38, at 20°C/min. gave the following specific heat values shown in the second column of Table III.

TABLE III - SPECIFIC HEATS OF ZINC

Temperature °C	Specific Heat, C_p Observed cal/g.atom/°C	Specific Heat, C_p Calculated cal/g.atom/°C
125.0	6.28	6.32
135.0	6.28	6.35
145.0	6.28	6.38
155.0	6.34	6.40
165.0	6.34	6.43
175.0	6.41	6.46
185.0	6.47	6.48

They may be compared with values in the third column, calculated from the equation (23)

$$C_p = 25.10 + 11 \times 10^{-3}T + \ldots \qquad (10)$$

valid over the range 0-300°C. T is measured in °C. The agreement is better than ± 1.5% over the range examined and the calibration factor E = 130.7 mcal/°C/min. is therefore considered valid for both heats of fusion and specific heat measurements.

X-ray Diffraction. X-ray diffraction powder photographs of samples contained in silica tubes, 0.5 mm diameter, were obtained with a North American Philips Co. powder camera using a Cu Kα source of radiation of wavelength (λ) of 1.5418 Å. Exposure times varied and the interplanar d spacings were calculated according to:

$$d = \frac{\lambda}{2 \sin \theta} \qquad (11)$$

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where θ is the angle subtended between pairs of symmetrical arcs. Cal-
culations were carried out on a Hewlet-Packard computer. Intensity of
arc was visually estimated on an arbitrary 1-10 scale taking the most
intense line as 10.

<u>Form Modification under Aqueous Conditions</u>. As a prelude to
further investigation, qualitative examination of possible changes in
form, either morphological or structural, of dyes I, II and III under
conditions of dyeing was carried out.

Exactly 0.03 gram of each dye (prepared as described on page
12) was made up as a 25.0 ml suspension in a 0.015% aqueous solution of a
dispersing agent, Triton X-100*, an alkylarylpolyethyleneoxide alcohol
of general formula, $R-Ar(OCH_2CH_2)_{9-10}OH$. The suspension was heated under
reflux at $85.3 \pm 0.1^{\circ}C$ in a thermostat bath and maintained at this temp-
erature for three hours with occasional shaking. During this time,
small samples were removed at intervals and examined microscopically. At
the end of this period, the samples were filtered, washed free from dis-
persing agent with water at room temperature and after drying at $< 60^{\circ}C$
examined by DSC, and in the case of dyes II and III by X-ray diffraction.

This procedure was also repeated for suspensions made up with
0.015% solutions of an anionic dispersing agent, Tamol N*, the sodium
sulphonate of a naphthalene-formaldehyde condensate and Retarder LAN**,
a cationic reagent of unknown structure.

*Available from Rohm and Haas Co., Philadelphia 5, Pa.

**Available from E. I. DuPont de Nemours Co., Inc., Wilmington, Delaware

RESULTS

For the purpose of later discussion, the results for each dye are presented in two main sections. In the first section, data on differential scanning calorimetry, visual observation and X-ray powder analysis for each dye are presented in that order. Heat capacity data for each dye are described in a second separate section since these data are treated in a different manner in discussion.

Section I - Differential Scanning Calorimeter Visual and X-ray Results

Dye I - C.I. Disperse Red 9 - 1-Methylaminoanthraquinone

This dye crystallizes from n-butanol as a polycrystalline pale red material consisting of long thin plates and needles with no regular habit. This form is shown in Figure 9a.

Several thermograms of this form of dye I were obtained at different heating rates using hermetically sealed containers. They show the shape of curve 1 in Figure 10. Only one phase change can be seen, that of melting at 169°C. However, on allowing the molten dye to cool and solidify and repeating the heating process, curve 2 was obtained, in which a second endothermic peak develops at 158°C. On additional recycling, curves 3 and 4 were obtained; no other change occurred and the two peaks, of approximately equal area, persisted.

For quantitative calorimetric data, the X-axis temperature scale must be that of the reference sample. Since the reference temperature is programmed in a linear manner, the plot of ΔT against temperature is equivalent to a time-based plot. The sample and reference positions must therefore be reversed. Slight differences in transition and melting temperatures were found when this procedure was adopted. Peak areas were determined in this manner for both the crystalline and melt-solidified dye. The molar enthalpy changes of transition or melting were determined from the equation,
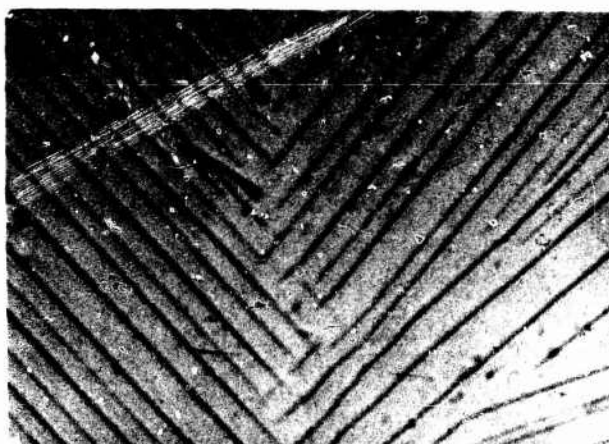
$$\Delta H = 130.7 \frac{A \Delta T_s T_s M}{ma} \tag{12}$$

where A is the peak area in sq. in., ΔT_s, the Y-axis sensitivity in °C/in., T_s, the X-axis sensitivity in °C/in., M is the formula weight, m the mass of sample in mg. and a is the heating rate in °C/min.

Enthalpies of transition and fusion for both forms of the dye are shown in Table IV.

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(a) X530
Recrystallized

(b) X530
Melt-solidified

Figure 9.   RECRYSTALLIZED AND MELT-SOLIDIFIED FORMS
OF C.I. DISPERSE RED 9